Name:____

Chemistry 3600 Fall, 2003
First Examination
October 3, 2003

Read over all the questions before you start to answer, as some are more difficult than others. Each question shows the number of points that it is worth in parenthesis. Show the formulas you used and all your work to get full credit. Express all answers with the correct number of sigfigs!

Formulas:

$$\bar{x} = \frac{\sum_i x_i}{n} \qquad s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}} \qquad \mu = \bar{x} \pm \frac{ts}{\sqrt{n}} \qquad F = \frac{s_1^2}{s_2^2} \qquad Q = \frac{\text{gap}}{\text{range}}$$

For $F_{calc} > F_{table}$

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s_1^2/n_1 + s_2^2/n_2}} \qquad d.f. = \left\{ \frac{(s_1^2/n_1 + s_2^2/n_2)^2}{\frac{(s_1^2/n_1)^2}{n_1+1} + \frac{(s_2^2/n_2)^2}{n_2+1}} \right\} - 2$$

For $F_{calc} < F_{table}$

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}} \qquad s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$$

Tables:

Q table @ 90% confidence:

Q	0.94	0.74	0.64	0.56	0.51	0.47	0.44	0.41
N	3	4	5	6	7	8	9	10

t table @ 95% confidence:

t	12.71	4.30	3.18	2.78	2.57	2.45	2.36	2.31	2.26
d.f.	1	2	3	4	5	6	7	8	9

F table @ 95% confidence:

d.f. (s_2)	*d.f.* (s_1)				
	2	3	4	5	6
2	19.00	19.16	19.25	19.30	19.33
3	9.55	9.28	9.12	9.01	8.94
4	6.94	6.59	6.39	6.26	6.16
5	5.79	5.41	5.19	5.05	4.95
6	5.14	4.76	4.53	4.39	4.28

1) List the steps involved in a chemical analysis (10)

Formulate the Question/Research
Design a Procedure/Research
Sampling
Sample Preparation
Analytical Method/Analysis
Data Analysis/Interpretation
Conclusions/Final Report

2) A 56.0 wt % solution of perchloric acid ($HClO_4$, MW=100.458 g/mol) has a density of 1.35 g/mL. (10 total)

a) What is the formal concentration of $HClO_4$? (5)

$$\frac{\mathbf{0.56\ g\ HClO_4}}{\mathbf{1g\ solution}}\times\mathbf{1.35\ g\ solution/mL}\times\frac{\mathbf{1mol}}{\mathbf{100.458\ g}}\times\frac{\mathbf{1000\ mL}}{\mathbf{L}}=\mathbf{7.53\ F}$$

b) Which is more accurate to state concentration in for this case, formality or molarity? Why? (5)

$HClO_4$ is a strong acid, completely dissociated in solution. Since there is no $HClO_4$ in solution to speak of, formal concentration is more accurate than molar concentration.

3) Repeated measurements of the zirconium concentration (Zr, 91.224 g/mol) from a soil sample gave values of 185.7, 177.4, 167.6, 181.45, and 189.3 ppm. (30 total)

a) What are the mean concentration, standard deviation, and 95% confidence interval of the Zr concentration? (10)

$$\bar{x}=\frac{\text{sum}}{n}=\frac{185.7+177.4+167.6+181.45+189.3}{5}=180.3$$

$$s=\sqrt{\frac{\sum(\bar{x}-x_i)^2}{n-1}}=\sqrt{\frac{(180.3-185.7)^2+(180.3-177.4)^2+(180.3-167.6)^2+(180.3-181.45)^2+(180.3-189.3)^2}{4}}=8.4$$

$$\mu=\bar{x}\pm\frac{ts}{\sqrt{n}}=180.3\pm\frac{(2.78)(8.4)}{\sqrt{5}}=180.3\pm10.4$$

b) Use the *Q*-test to determine if the lowest measurement can be dropped from the set with 90% confidence. (10)

$$Q_{calc}=\frac{\text{Gap}}{\text{Range}}=\frac{177.4-167.6}{189.3-167.6}=0.45$$

$$Q_{table}=0.64>Q_{calc}$$

Therefore, the measurement cannot be dropped.

c) A second soil sample analyzed 6 replicate times for Zr content gave mean=0.0195 % and standard deviation=0.00208 %. At the 95% confidence level, does this soil sample differ in Zr concentration from the soil sample in part (a)? (10)

0.0195%, 0.00208% = 195 ppm, 20.8 ppm →→→x_1=195, s_1=20.8, n_1=6; x_2=180.3, s_2=8.4, n_2=5

$$F_{calc}=\frac{s_1^2}{s_2^2}=\frac{20.8^2}{8.4^2}=6.13 \qquad t_{calc}=\frac{|\bar{x}_1-\bar{x}_2|}{\sqrt{s_1^2/n_1+s_2^2/n_2}}=\frac{|195-180.3|}{\sqrt{(20.8^2/6)+(8.4^2/5)}}=1.58$$

$$F_{table}=6.26>F_{calc} \qquad \text{d.f}=7.6\ \text{(from equation)}\ t_{table}=2.26>F_{calc}$$

Therefore, there is no significant difference in the samples

***Note**: I screwed up some of the numbers here because I wanted to have you get $F_{calc}>F_{table}$ to use the 2nd set of t-equations. But, the bottom line is you needed to do an F-test and then a t-test to get full credit on the problem.*

4) Aluminum hydroxide, $Al(OH)_3$ *(s)* (MW=78.003) has a K_{sp} of $5.81x10^{-33}$. (30 total)

a) How many nanograms of $Al(OH)_3$ will dissolve in 1.00 L of pure water? (10)

$$\mathbf{Al(OH)_3\,(s) \leftrightarrow Al^{3+}\,(aq) + 3OH^-\,(aq)}$$

$$\mathbf{K_{sp} = 5.81\times10^{-33} = [Al^{3+}][OH^-]^3} \quad x=[Al^{3+}]$$

$$\mathbf{27x^4 = 5.81\times10^{-33} \Rightarrow x = 3.83\times10^{-9}\,M = \frac{mol}{L}\times\frac{78.003\,g}{mol} = 2.99\times10^{-7}\,g = 299\,ng}$$

b) Aluminum can also form a series of complex ions in solution with hydroxide: $Al(OH)^{2+}$*(aq)*, $\beta_1=1.0x10^9$; $Al(OH)_2^+$*(aq)*, $\beta_2=5.0x10^{18}$; $Al(OH)_3$*(aq)*, $\beta_3=1.0x10^{27}$; $Al(OH)_4^-$, $\beta_4=1.1x10^{33}$. Calculate the concentration of Al^{3+}*(aq)* **and** all four complex ions in a solution containing $Al(OH)_3$*(s)* where the pH is held constant at 7.8. (20)

pOH=14-7.8=6.2→→→$[OH^-]$=-log pOH=$10^{-6.2}$=$6.31x10^{-7}$ M

$[Al^{3+}]=Ksp/[OH^-]^3=(5.81x10^{-33})/(6.31x10^{-7})^3=2.31x10^{-14}$ M

$[Al(OH)^{2+}]=\beta\,[Al^{3+}][OH^-]= (1x10^9)(2.31x10^{-14})(6.31x10^{-7})=1.5x10^{-11}$ M

$[Al(OH)_2^+]=\beta_2\,[Al^{3+}][OH^-]^2= (5.0x10^{18})(2.31x10^{-14})(6.31x10^{-7})^2=4.6x10^{-8}$ M

$[Al(OH)_3]=\beta_3\,[Al^{3+}]\,[OH^-]^3= (1.0x10^{27})(2.31x10^{-14})(6.31x10^{-7})^3=5.8x10^{-6}$ M

$[Al(OH)_4^-]=\beta_4\,[Al^{3+}]\,[OH^-]^4= (1.1x10^{33})(2.31x10^{-14})(6.31x10^{-7})^4=4.0x10^{-6}$ M

5) Identify each of the following chemical species as a strong acid, strong base, weak acid, weak base, or none of the above. (10 total)

a) Ammonium (NH_4^+)

Weak acid

b) Bromide ion (Br^-)

none

c) Hydrogen iodide (HI)

Strong acid

d) Oxalate ion ($C_2O_4^{2-}$)

Weak base

e) Tetraethylammonium hydroxide $(CH_3CH_2)_4N^+OH^-$

strong base

6) Diprotic sulfurous acid (H_2SO_3) is a weak acid unlike its cousin sulfuric acid. H_2SO_3 has a K_{a1}=1.3x10^{-2} and a K_{a2}=5.1x10^{-6}. (10 total)

a) Write the association reactions for the ***conjugate base*** forms of sulfurous acid in water (5)

$$\mathbf{SO_3^{2-} + H_2O \leftrightarrow HSO_3^- + OH^- \qquad K_{b1}}$$

$$\mathbf{HSO_3^- + H_2O \leftrightarrow H_2SO_3 + OH^- \qquad K_{b2}}$$

b) Determine the K_{b1} and K_{b2} equilibrium constants for the reactions in part (a) (5)

$$K_{b1} = \frac{K_w}{K_{a2}} = \frac{1\times10^{-14}}{5.1\times10^{-6}} = 2.0\times10^{-9} \qquad K_{b2} = \frac{K_w}{K_{a1}} = \frac{1\times10^{-14}}{1.3\times10^{-2}} = 7.7\times10^{-13}$$